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ULTRAVIOLET AND VISIBLE SPECTRA OF TACOT
(TETRANITRODIBENZO-1,3a,4,6a-TETRAAZAPENTALENE)
IN VARIOUS SOLVENTS

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Frankford Arsenal
Philadelphia, Pennsylvania

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The ultraviolet and visible spectra of Tacot (tetranitrodibenzo-1,3a,4,6a-tetraazapentalene) were determined in nine solvents in which the material was significantly soluble. These solvents were sulfuric acid, perchloric acid, nitric acid, glycerin, dimethylsulfoxide, ammonium hydroxide, morpholine, piperidine, triethanolamine, and N,N-dimethylformamide. The first five of these solvents gave orange solutions while the last four gave amber (continued)			

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20. ABSTRACT: (continued)

or other dark-colored solutions; however, the colors of all the solutions after aliquoting and diluting prior to the spectral measurements were yellowish. The study in the ultraviolet region was limited by the relatively high cut-off points of some of the solvents. The molar absorptivities of the peaks were calculated. A somewhat arbitrary grouping of the peaks according to location showed that peaks occurred for Tacot in all solvents at 450 to 506 nm except for piperidine which showed a rising slope and significant absorption in this region. Sulfuric acid showed a strong peak at 416 nm. Sulfuric acid, morpholine, and piperidine showed peaks in the area of 395 to 403 nm (peaks did not occur in this region in the other solvents). A peak occurred at 318 to 350 nm for all the solvents except nitric acid and piperidine (which were not useable in this range). A peak occurred at 248 to 281 nm in sulfuric acid, perchloric acid, and ammonium hydroxide (the only solvents useable in this range). The solvents that originally gave orange solutions were inclined to give sharper peaks, while the solutions that originally gave amber and other dark-colored solutions were frequently inclined to give shoulders and plateaus. The colors obtained from the orange solutions tended to be more stable. The extraordinary effect of the solvent on the spectrum of Tacot is probably related to the tendency of Tacot to form complexes with the solvent. Experiments indicated that Tacot could be determined quantitatively by measurement of the color in sulfuric acid, perchloric acid, nitric acid, and dimethylsulfoxide at 416, 486, 487, and 506 nm, respectively. The method could not be applied to the determination of Tacot in primers because of the difficulty of completely extracting the Tacot from the primers and also because the other ingredients of primers interfered with the color.

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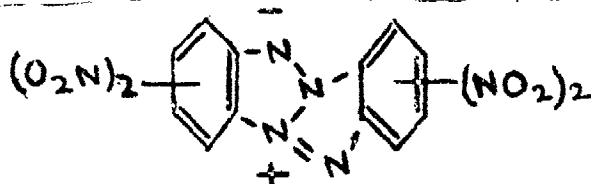
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INTRODUCTION

Tacot is tetranitrodibenzo-1,3a,4,6a-tetraazapentalene.¹⁻⁴ The molecular formula of the material is $C_{12}H_4N_8O_8$ and its structural formula is as follows:



In appearance Tacot is an orange powder. It is used in priming compositions and detonators that are subject to high temperatures as in rockets and space vehicles.¹⁻³ Tacot is effective for such a purpose because it continues to function as an explosive even when heated to as high a temperature as 400°C (the melting point of the material).¹⁻³

Tacot is made by a process patented by duPont Co.¹⁻³ that involves nitration of dibenzo-1,3a,4,6a-tetraazapentalene with fuming nitric acid.¹⁻⁴ The production of the parent compound, dibenzo-1,3a,4,6a-tetraazapentalene, is also covered by duPont Co. patents.³⁻⁵

Not much has been reported on the solubility of Tacot. It has been stated² that the material is soluble in 95% nitric acid and that it is insoluble in water, most acids, and organic solvents and only slightly soluble in nitrobenzene, dimethylformamide, and acetone. Apparently, there is little information in the literature on the ultraviolet and visible spectra.

EXPERIMENTAL

The solubilities of Tacot in various solvents was investigated by adding 0.01 g of Tacot to about 75 ml of the solvent and noting whether the Tacot dissolved after a few minutes occasional stirring.

¹Chemical and Engineering News, Nov 5, 1962, 49-50.

²E. I. duPont de Nemours and Co., "Technical Information on duPont Explosives Specialties, Tacot, Properties," New York, N. Y.

³R. A. Carboni (to E. I. duPont de Nemours and Co.) U. S. Patent 2,904,544, Sept 15, 1959; RE 25,238, Sept 11, 1962.

⁴R. A. Carboni, J. C. Kauer, W. R. Hatchard, and R. J. Harder, J. Am. Chem. Soc., 89, 2626 (1967).

⁵R. A. Carboni, J. C. Kauer, J. E. Casale, and H. E. Simmons, J. Am. Chem. Soc. 89, 2618 (1967).

By this means it was found that Tacot was not significantly soluble in the following solvents: water, hydrochloric acid, phosphoric acid, ethyl ether, petroleum ether, carbon tetrachloride, and isopropyl alcohol. Tacot was only slightly soluble in the following solvents, with the production of a yellowish or yellowish-green fluorescence: methyl alcohol, ethyl alcohol, butyl alcohol, acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, dioxane, methylene chloride, chloroform, bromoform, benzene, toluene, xylene, ethyl acetate, butyl acetate, amyl acetate, triacetin, tricresyl phosphate, formic acid, acetic acid, acetic anhydride, nitrobenzene, amyl nitrate, acetaldehyde, aniline, thiophene, acetonitrile, and pyridine. The 0.01 g of Tacot dissolved in the following solvents with the production of the indicated colors:

sulfuric acid - orange
 perchloric acid - orange
 nitric acid - orange
 glycerin ($C_3H_5(OH)_3$) (required heating to about $50^{\circ}C$) - orange
 dimethylsulfoxide $\{(CH_3)_2SO\}$ - orange
 sodium hydroxide solution (20%) - amber
 ammonium hydroxide - amber
 morpholine $\{OCH_2CH_2NHCH_2CH_2\}$ - amber
 piperidine $\{CH_2CH_2CH_2CH_2CH_2NH\}$ - amber
 triethanolamine $\{(HOCH_2CH_2)_3N\}$ - brownish-red
 N,N-dimethylformamide $\{HCON(CH_3)_2\}$ - yellowish-brown with
 olive-green tint

The visible and ultraviolet spectra for Tacot were determined for all the above solvents in which Tacot was soluble except the sodium hydroxide solution (no spectral work was done with the latter solution because of the danger of attacking the spectrophotometer cells). The sulfuric acid, perchloric acid, and ammonium hydroxide used for the spectral studies were reagent grade, while the other solvents were Fisher Certified Reagents. The Tacot was obtained from duPont Co. The spectra were prepared using a Cary Model 15 spectrophotometer (1-cm cell) with the solvent in the reference cell. For all the solvents except glycerin, 0.0100g of Tacot was weighed on a semi-micro balance into a 100-ml beaker, then about 75 ml of the solvent was added and the Tacot was dissolved by stirring with a stirring rod at room temperature. The solution was diluted to 100 ml in a volumetric flask with the solvent, an appropriate aliquot (or sub-aliquot) was pipetted into a 50-ml volumetric flask, the volume was brought up to 50 ml, and the spectrum was determined. In the case of the glycerin, the Tacot was dissolved by warming at about $50^{\circ}C$, the solution was diluted to 200 ml, and the aliquot was taken. All the solutions after the final dilution prior to the spectral readings were yellowish in color.

The spectra obtained for Tacot in the different solvents are shown in Figures 1 to 10. The spectra are given from the cut-off point of the solvent to 600 nm (no significant absorbance was obtained above 600 nm). The cut-off points of the solvent were determined by obtaining the spectra of the solvents against water (Figures 11 to 20) and ascertaining the wave length at which the absorbance was approximately 0.5.⁶ The cut-off points of the solvents are given in Table I.

A summary of the data concerning the location of the peaks and the molar absorptivities (ϵ = molecular weight of Tacot/cell width x conc. in g/l) are shown in Table I.

DISCUSSION AND RESULTS

There was no clear-cut pattern as to why Tacot was soluble in some solvents and insoluble in others. It would seem that some strong inorganic acids are solvents for the material as are certain alkaline reagents (both inorganic and organic). The solvents glycerin and dimethylsulfoxide are ordinarily not considered to be acidic or basic. All the solvents in which Tacot is soluble can be considered to be polar.

As indicated in Table I, the peaks in many cases were not clear-cut but occur as shoulders and plateaus. In order to assess possible patterns, the peaks were grouped together somewhat arbitrarily according to location. By this means it is seen that peaks occurred at 450 to 506 nm in all the solvents except piperidine which showed a rising slope and significant absorbance in this region. Sulfuric acid showed a strong peak at 416 nm. Sulfuric acid, morpholine, and piperidine showed peaks at 395 to 450 nm (peaks did not occur in this region with the other solvents). A peak occurred at 318 to 350 nm for all the solvents except nitric acid and piperidine (which were not usable in this range). A peak occurred at 248 to 281 nm in sulfuric acid, perchloric acid, and ammonium hydroxide (the only solvents usable in this range).

An attempt was made to compare the spectra obtained from the solvents that gave orange solutions with the solvents that gave amber or other dark-colored solutions (all the solutions finally used for this spectral work were yellowish as previously noted). The only conclusion that could be drawn was that the solvents that originally gave orange solutions were inclined to give sharper peaks while the solutions that originally gave amber or other dark-colored solutions were

⁶G. W. Ewing, "Instrumental Methods of Chemical Analysis," 2nd ed., p. 61, McGraw-Hill, New York.

frequently inclined to give shoulders and plateaus. The colors obtained with the orange solutions were more stable than the colors obtained with the amber and other dark-colored solutions.

Tacot and its parent compound are hybrids of several dipolar resonance structures,^{3-5,7} hence the interpretation of the spectrum of Tacot from the viewpoint of electronic configuration would be very difficult. Probably the diversity of the spectra is due to the tendency of Tacot to form complexes with the solvents.

A study was made of the possible application of the color obtained with Tacot in solution to the determination of Tacot. It was found that satisfactory straight-line calibration curves (using a Beckman Model B spectrophotometer) were obtained for sulfuric acid, perchloric acid, nitric acid, and dimethylsulfoxide at 416, 486, 487, and 506 nm, respectively. Glycerin was not satisfactory because of its viscosity. The colors obtained with the other solvents were not satisfactory for quantitative work since the colors changed somewhat with time.

The spectrophotometric determination of Tacot in primers was investigated. It was found that Tacot could not be completely extracted from the primers by sulfuric acid, nitric acid, or dimethylsulfoxide (perchloric acid was not used because of possible hazard). Also, it was found that the other ingredients of the primers (potassium chlorate, antimony sulfide, and calcium silicide) seemed to effect the color somewhat. Prior extraction of the primers with water (to remove the potassium chlorate) was not helpful. Possibly, the spectrophotometric technique could be used to determine Tacot in materials other than primers.

SUMMARY

The ultraviolet and visible spectra of Tacot (tetranitrodibenzo-1,3a,4,6a-tetraazapentalene) were determined in nine solvents in which the material was significantly soluble. These solvents were sulfuric acid, perchloric acid, nitric acid, glycerin, dimethylsulfoxide, ammonium hydroxide, morpholine, piperidine, triethanolamine, and N,N-dimethylformamide. The first five of these solvents gave orange

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⁵R. A. Carboni, J. C. Kauer, J. E. Castle, and H. E. Simmons, J. Am. Chem. Soc., 89, 2618 (1967).

⁷Y. T. Chia and H. E. Simmons, J. Am. Chem. Soc., 89, 2638 (1967).

solutions while the last four gave amber or other dark-colored solutions; however, the colors of all the solutions after aliquoting and diluting prior to the spectral measurements were yellowish. The study in the ultraviolet region was limited by the relatively high cut-off points of the solvents. The molar absorptivities of the peaks were calculated. A somewhat arbitrary grouping of the peaks according to location showed that peaks occurred for Tacot in all solvents at 450 to 506 nm except for piperidine which showed a rising slope and significant absorption in this region. Sulfuric acid showed a strong peak at 416 nm. Sulfuric acid, morpholine, and piperidine showed peaks in the area of 395 to 403 nm (peaks did not occur in this region in the other solvents). A peak occurred at 318 to 350 nm for all the solvents except nitric acid and piperidine (which were not usable in this range). A peak occurred at 248 to 281 nm in sulfuric acid, perchloric acid, and ammonium hydroxide (the only solvents usable in this range). The solvents that originally gave orange solutions were inclined to give sharper peaks, while the solutions that originally gave amber and other dark-colored solutions were frequently inclined to give shoulders and plateaus. The colors obtained from the orange solutions tended to be more stable. The extraordinary effect of the solvent on the spectrum of Tacot is probably related to the tendency of Tacot to form complexes with the solvent. Experiments indicated that Tacot could be determined quantitatively by measurement of the color in sulfuric acid, perchloric acid, nitric acid, and dimethylsulfoxide at 416, 486, 487, and 506 nm, respectively. The method could not be applied to the determination of Tacot in primers because of the difficulty of completely extracting the Tacot from the primers and also because the other ingredients of primers interfered with the color.

RECOMMENDATIONS

It is recommended that the investigatory work on Tacot be continued in order to establish a method for the assay of the material using wet chemical or instrumental techniques. Also, it is recommended that the infrared spectrum and thermal properties (using differential scanning calorimetry and thermogrametric analysis) be studied.

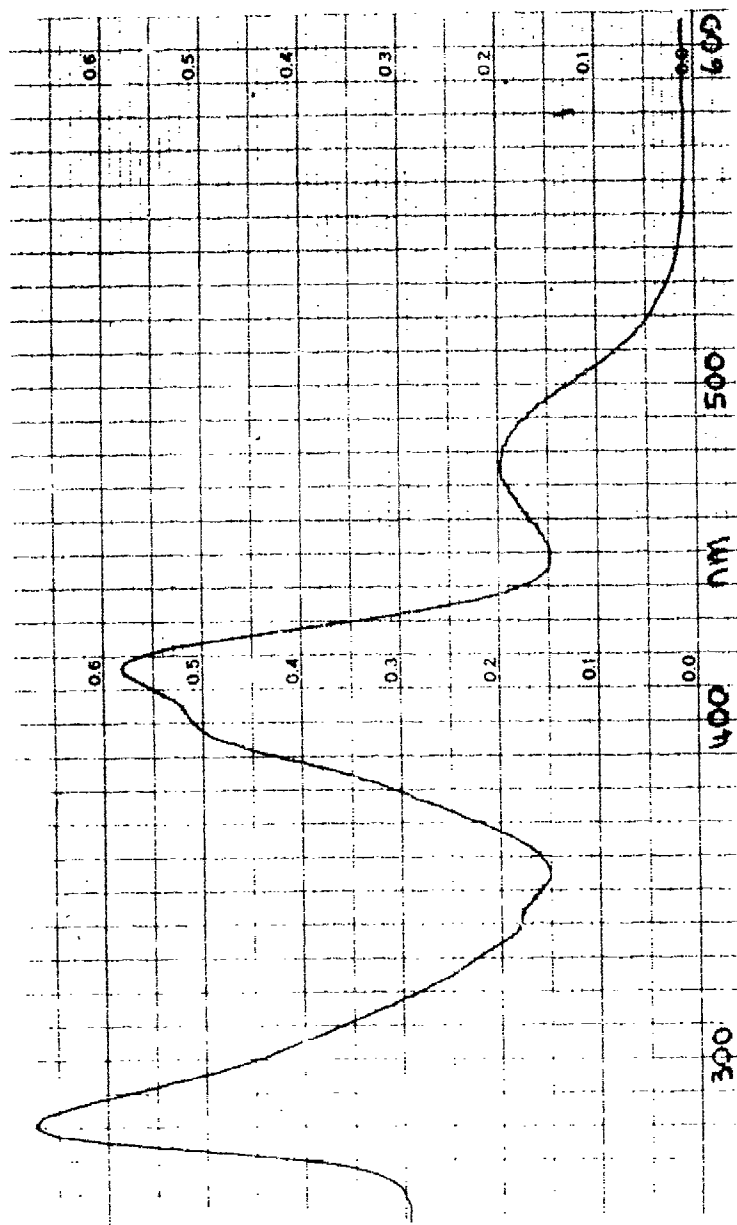


Figure 1. Spectrum of Tacot in Sulfuric Acid (vs Sulfuric Acid)

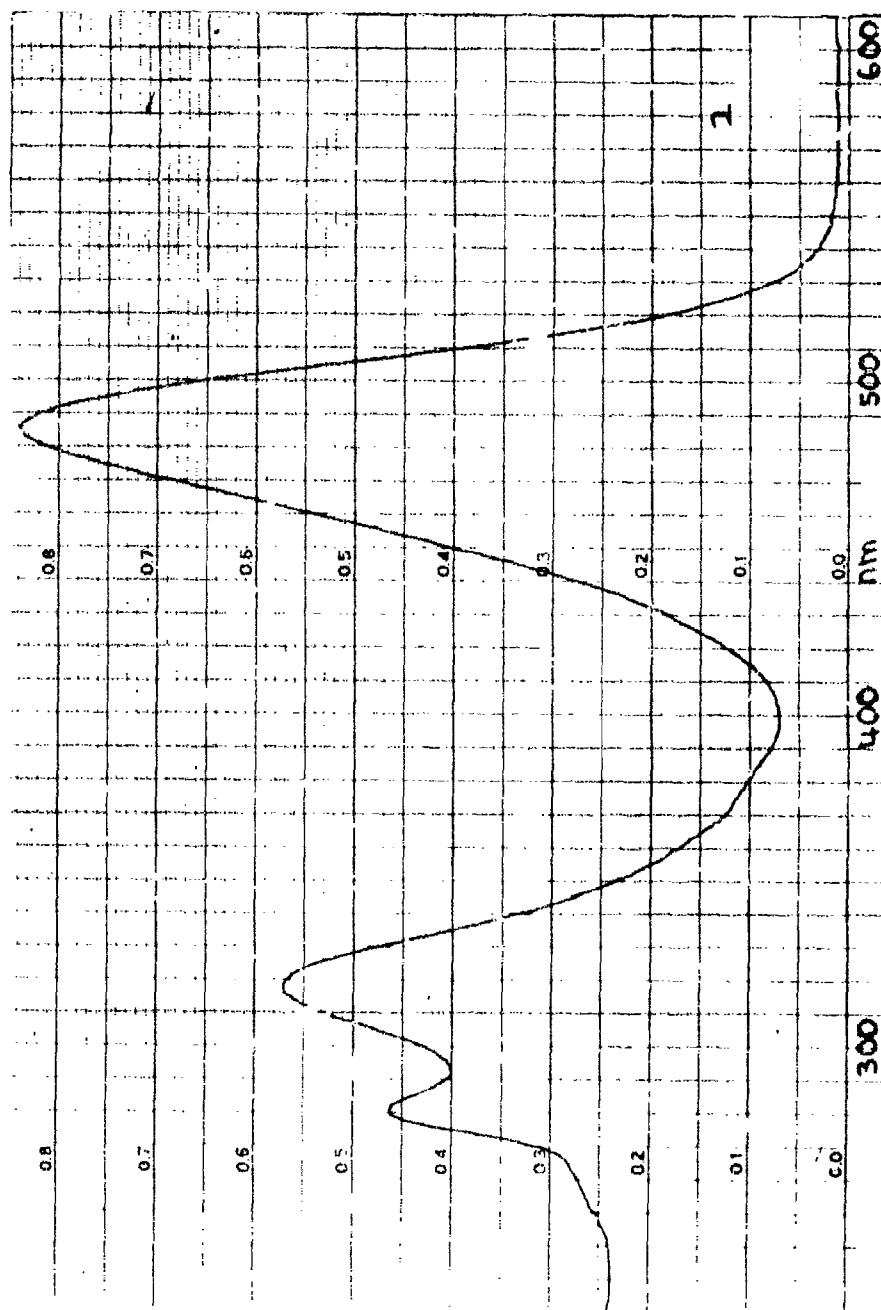


Figure 2. Spectrum of Tacot in Perchloric Acid (vs Perchloric Acid)

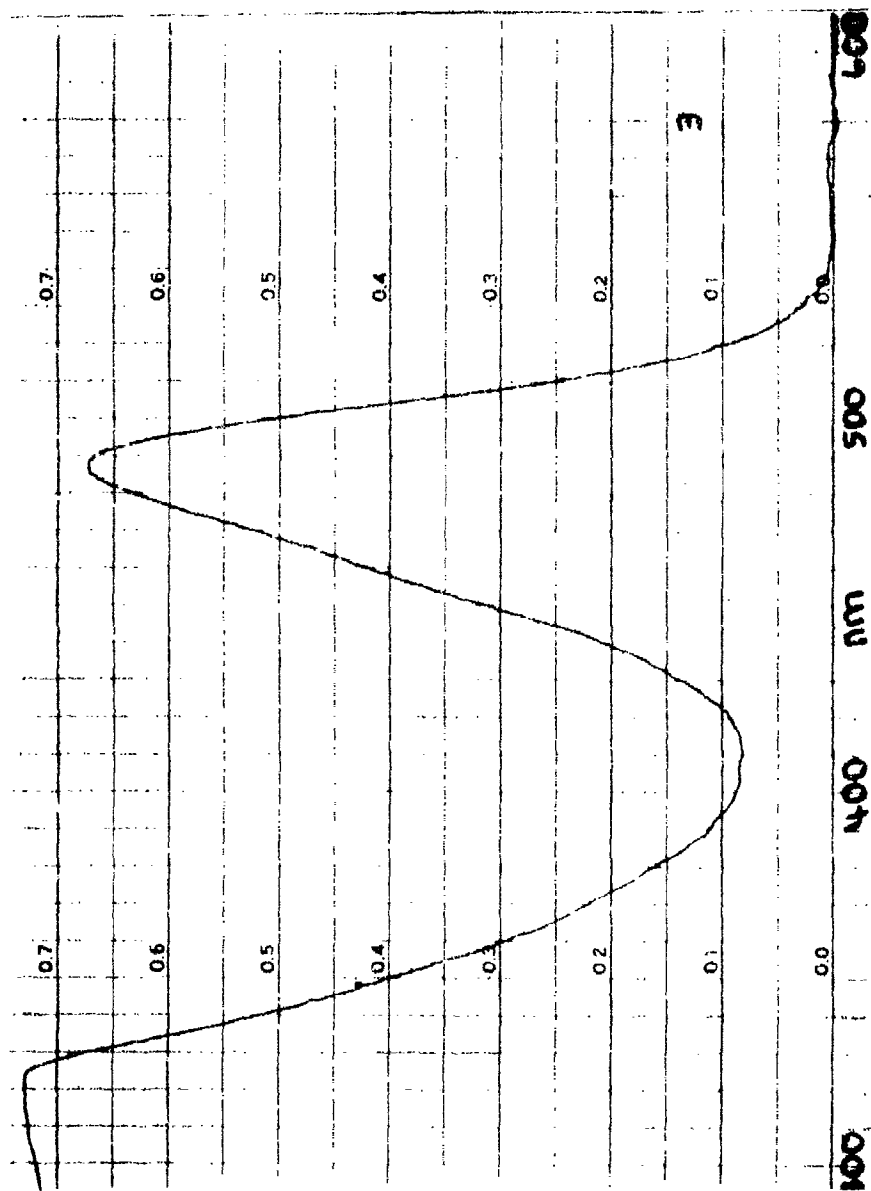


Figure 3. Spectrum of Tacot in Nitric Acid (vs Nitric Acid)

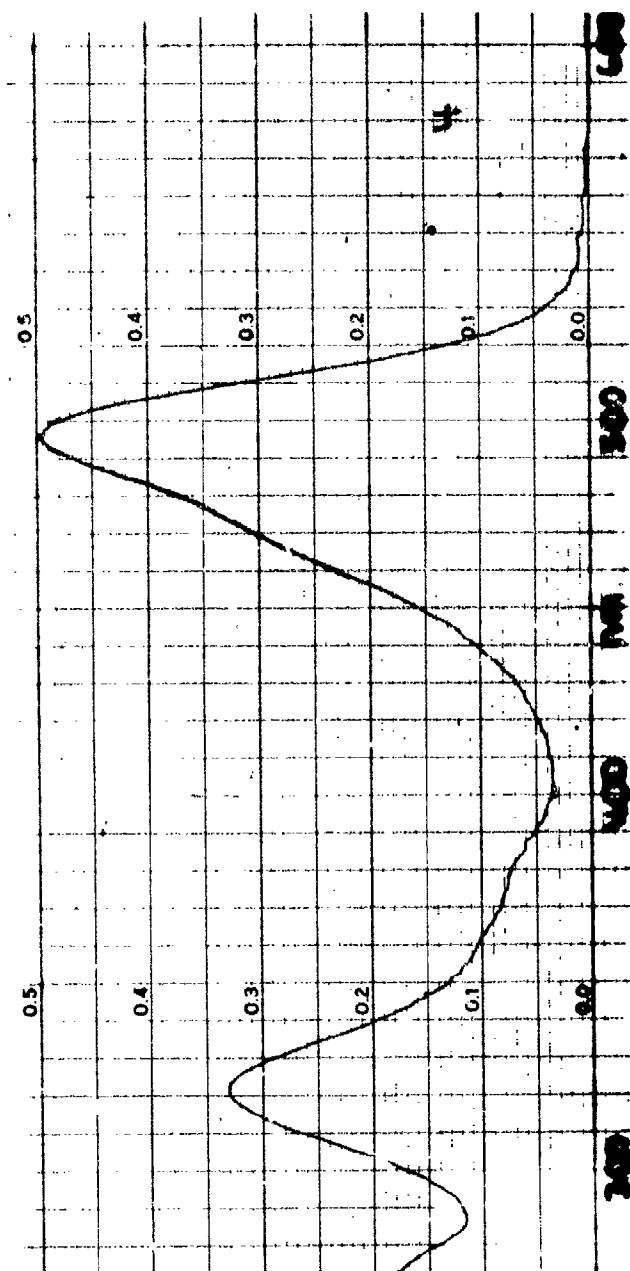


Figure 4. Spectrum of Tacot in Glycerin (vs Glycerin)

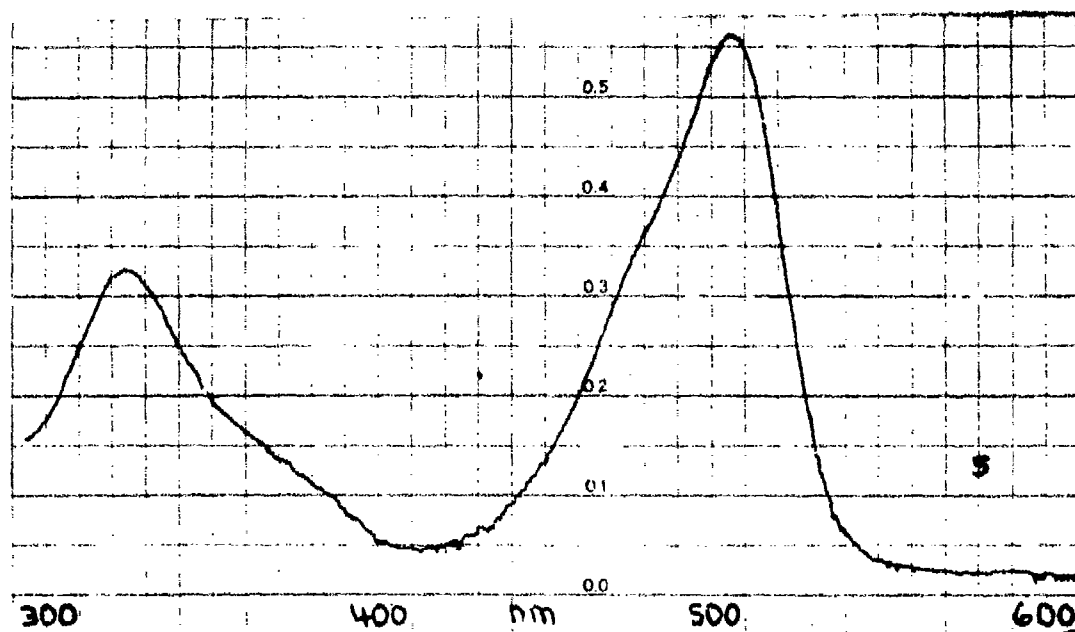


Figure 5. Spectrum of Tacot in Dimethylsulfoxide
(vs Dimethylsulfoxide)

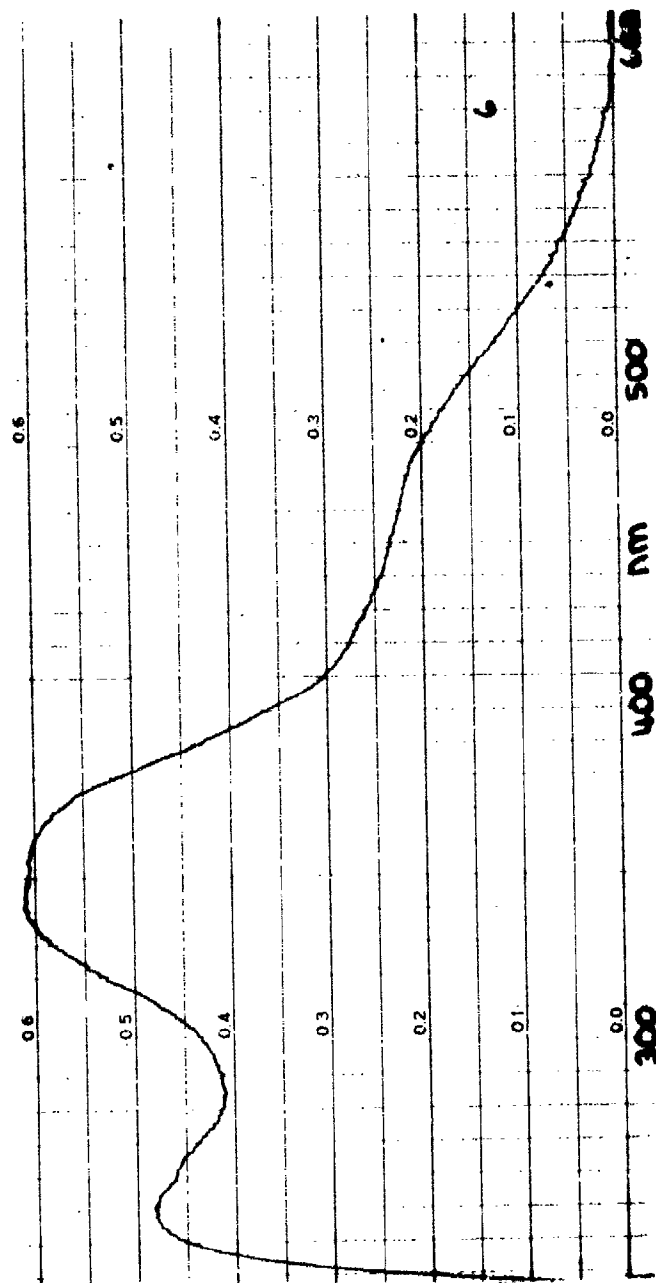


Figure 6. Spectrum of Tacot in Ammonium Hydroxide (vs Ammonium Hydroxide)

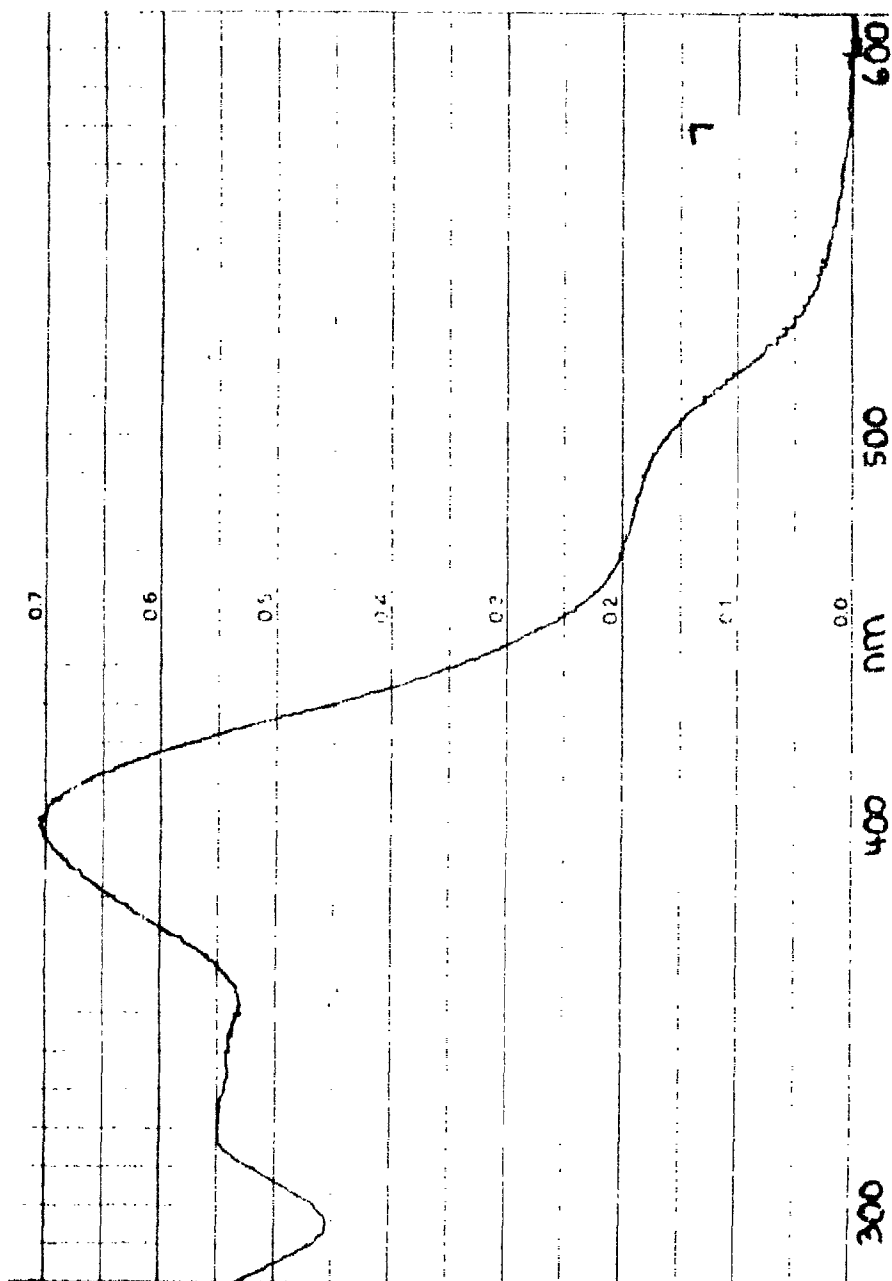


Figure 7. Spectrum of Tacot in Morpholine (vs Morpholine)

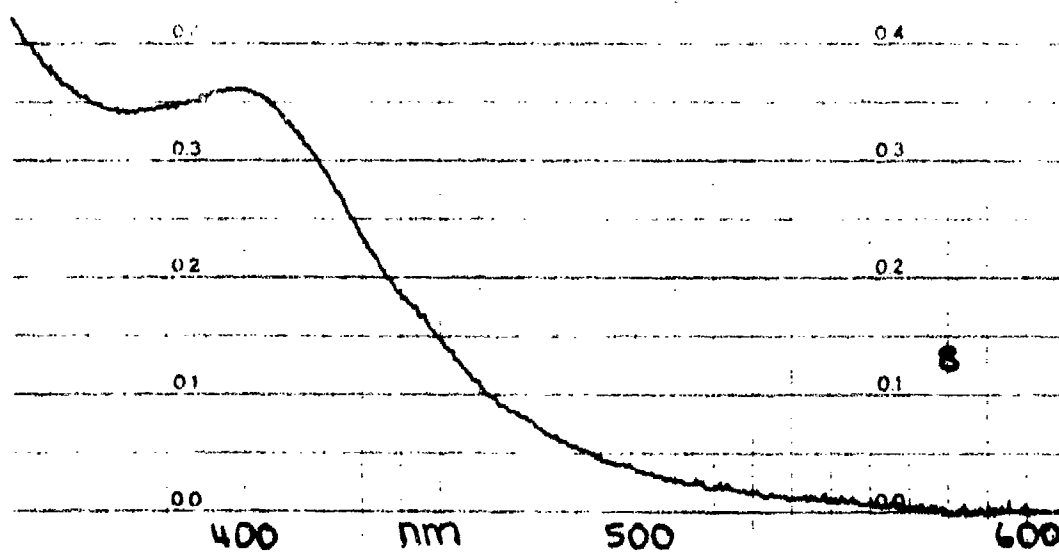


Figure 8. Spectrum of Tacot in Piperidine (vs Piperidine)

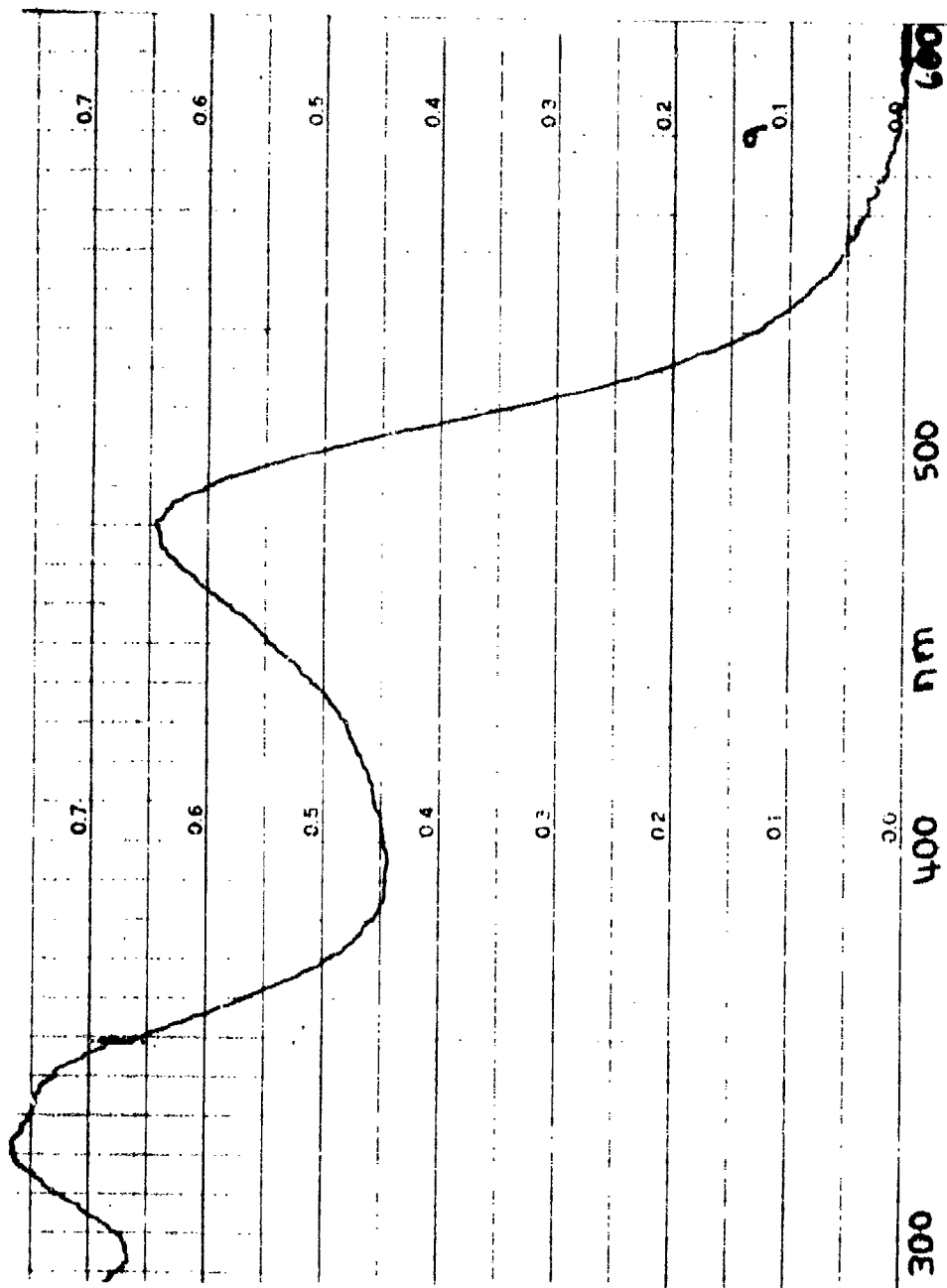


Figure 9. Spectrum of Tacot in Triethanolamine (vs Triethanolamine)

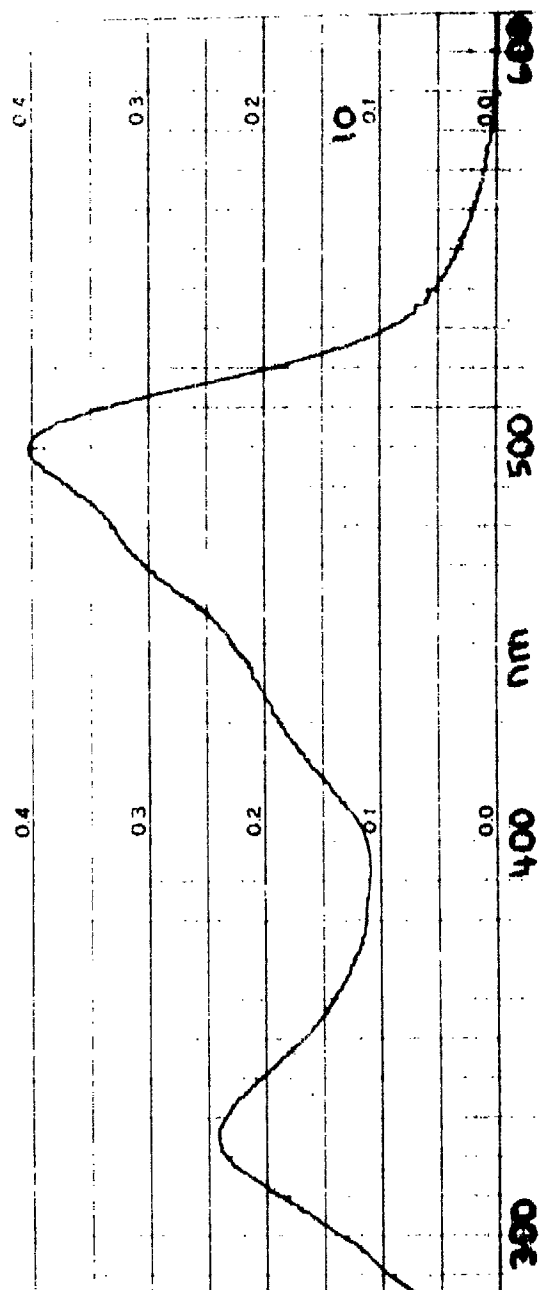


Figure 10. Spectrum of Tacot in N,N-Dimethylformamide (vs N,N-Dimethylformamide)

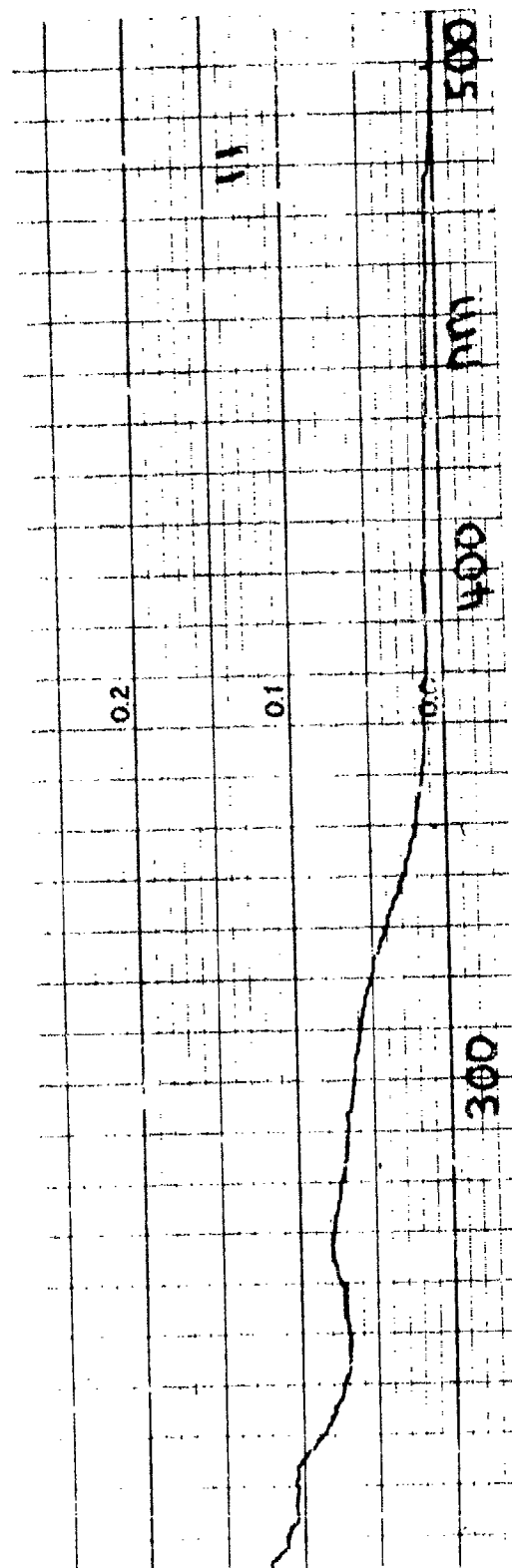


Figure 11. Spectrum of Sulfuric Acid (va Water)

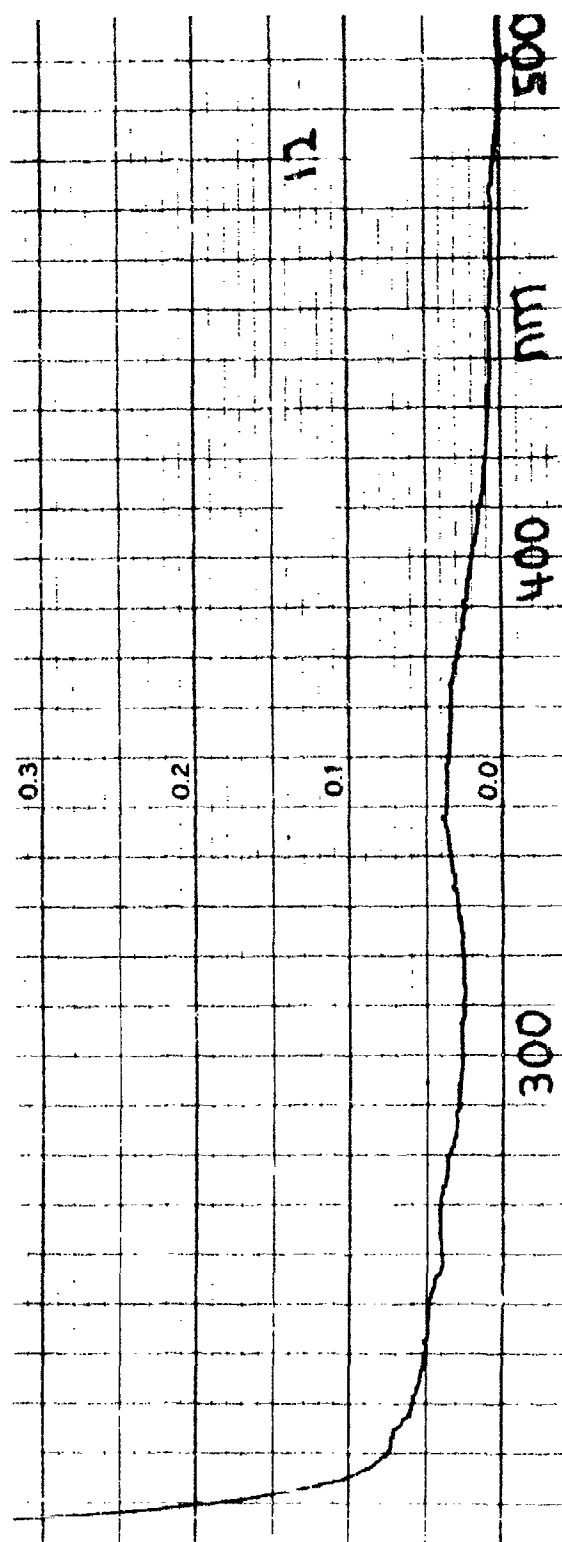


Figure 12. Spectrum of Perchloric Acid (vs Water)

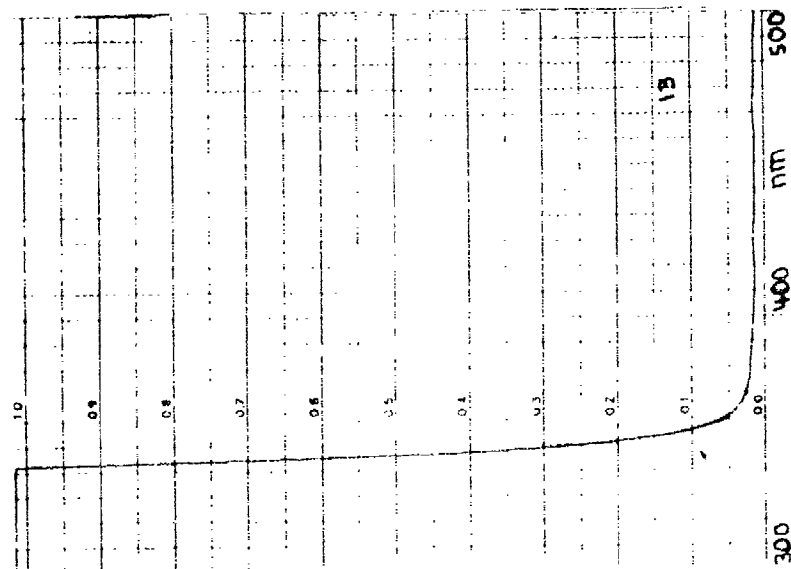


Figure 13. Spectrum of Nitric Acid (vs Water)

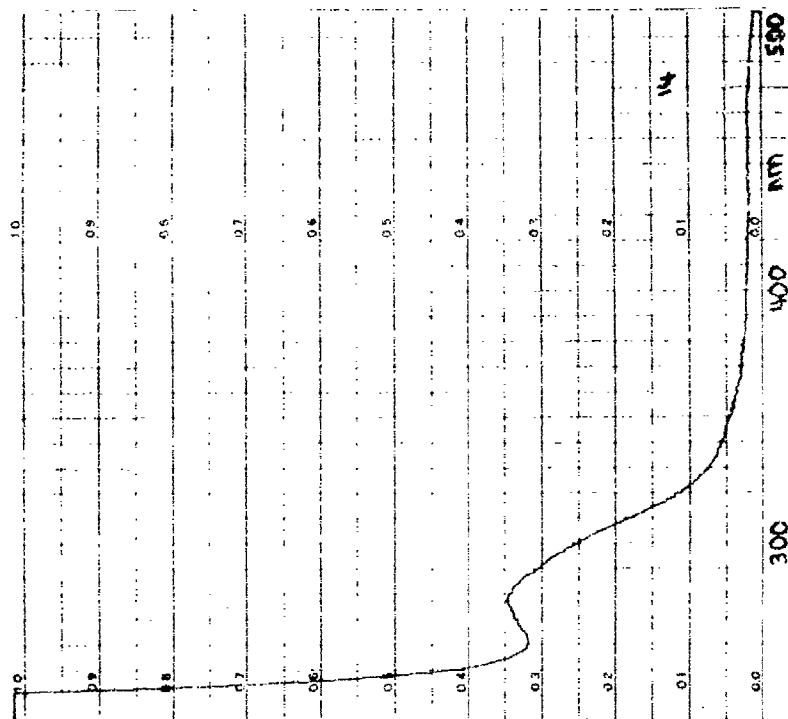


Figure 14. Spectrum of Glycerin (vs Water)

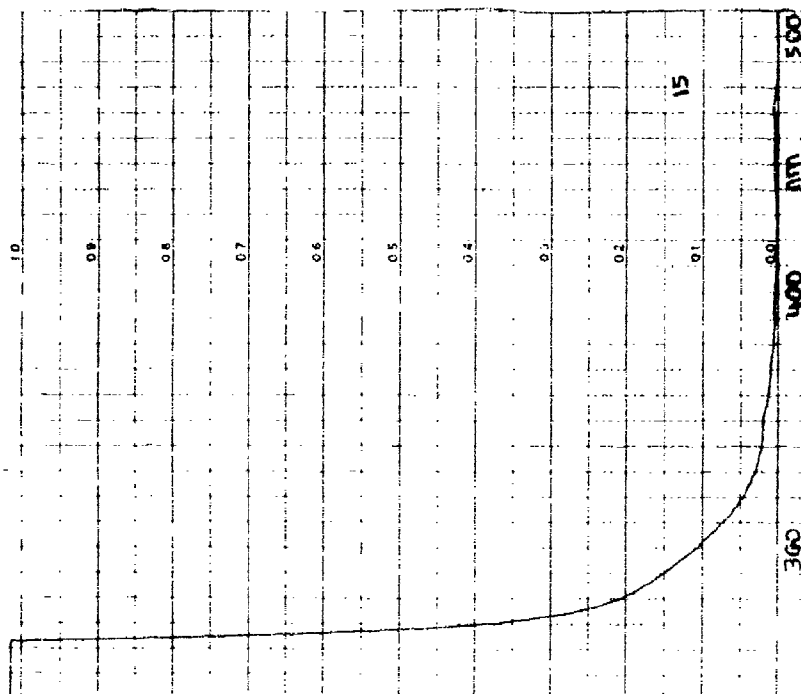


Figure 15. Spectrum of Dimethylsulfoxide
(vs Water)

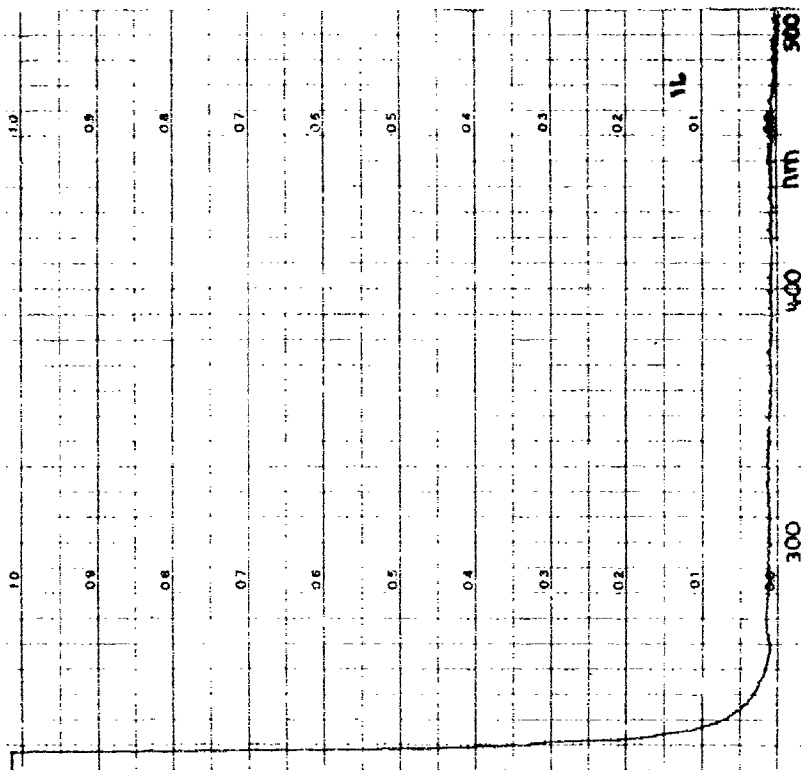


Figure 16. Spectrum of Ammonium Hydroxide
(vs Water)

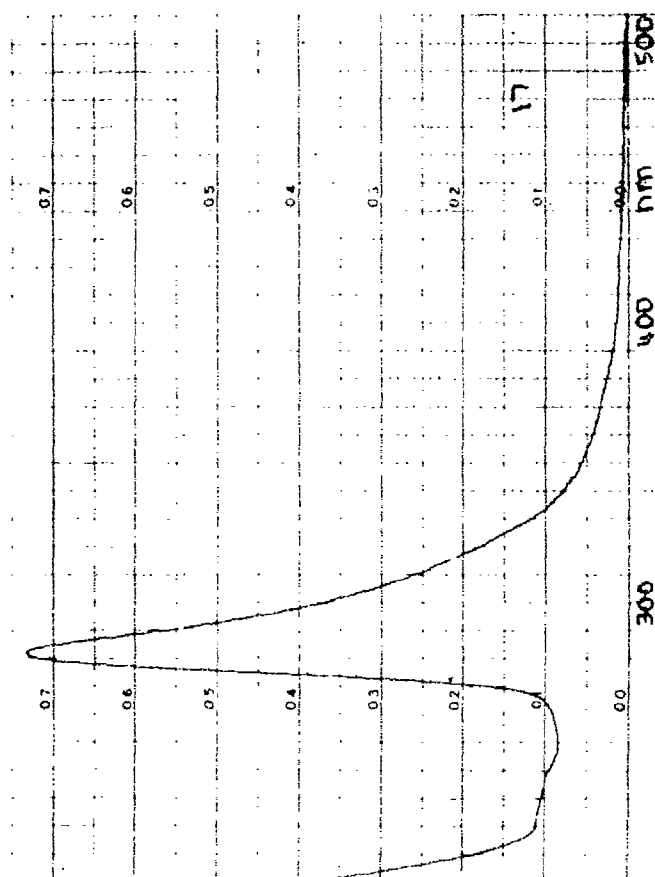


Figure 17. Spectrum of Morpholine (vs Water)

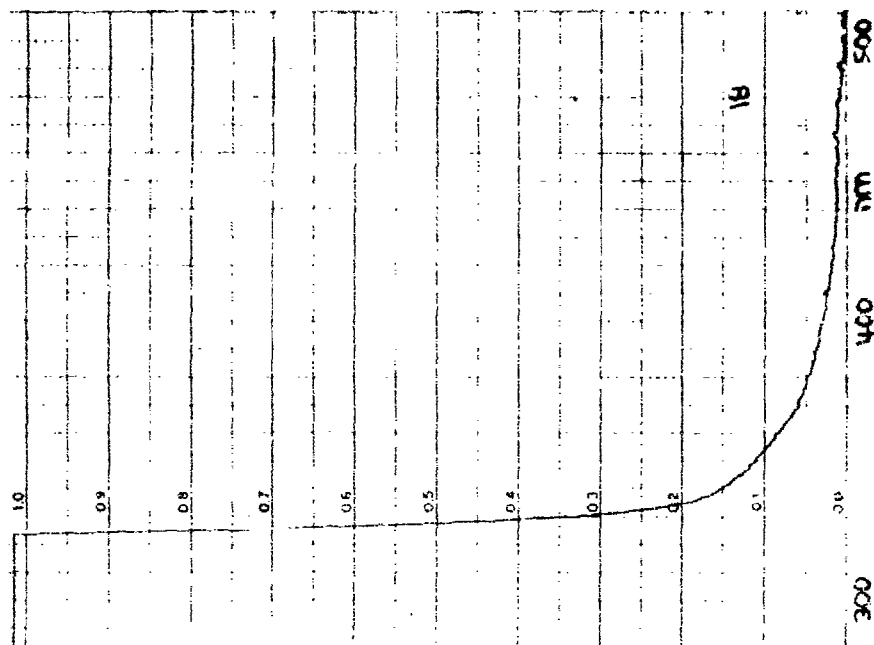


Figure 18. Spectrum of Piperidine (vs Water)

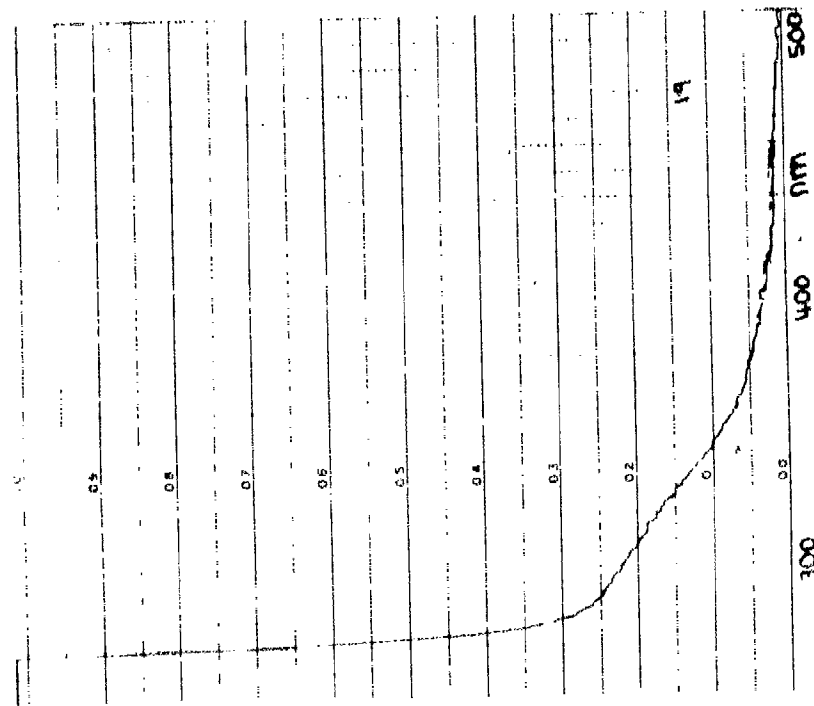


Figure 19. Spectrum of Triethanolamine
(vs Water)

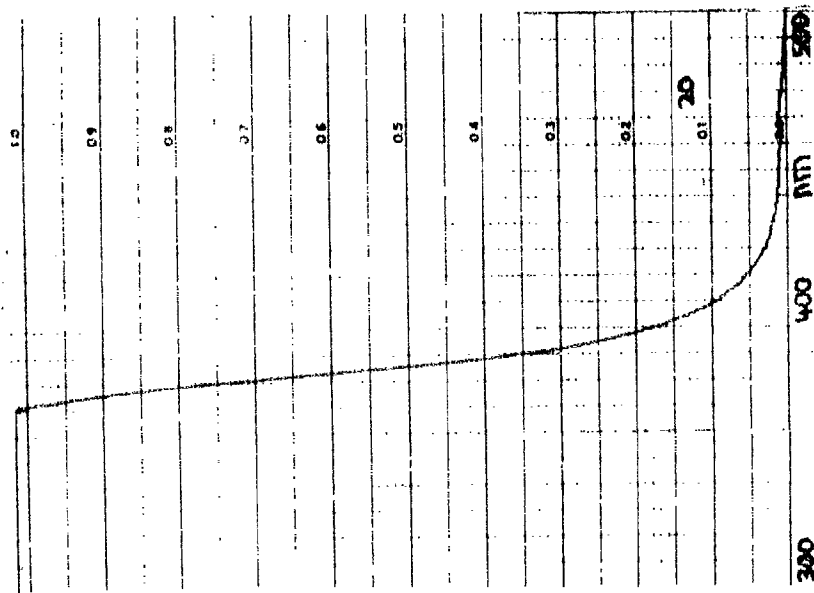


Figure 20. Spectrum of N,N-Dimethyl-
formamide (vs Water)

Table I.
Peaks of Tacot in Different Solvents

Solvent	Conc. of Tacot (mg/ml)	Peaks (cm)				
Sulfuric acid	0.01	475 ($\epsilon = 7579$)	415 ($\epsilon = 22500$)	403 (shoulder) ($\epsilon = 19800$)	345 (shoulder) ($\epsilon = 6990$)	281 ($\epsilon = 24100$)
Perchloric acid	0.01	486 ($\epsilon = 32300$)			318 ($\epsilon = 22100$)	281 ($\epsilon = 17900$)
Nitric acid	0.005	487 ($\epsilon = 52000$)				
Glyceric	0.0125	496 ($\epsilon = 15400$)				
Dimethylsulfoxide	0.005	505 ($\epsilon = 43500$)			322 ($\epsilon = 10300$)	
Ammonium hydroxide	0.01	~ 450 (plateau) (peak not clearly defined)			324 ($\epsilon = 23700$)	
Morpholine	0.01	~ 490 (plateau) (peak not clearly defined)		398 ($\epsilon = 21400$)	350 (very broad) ($\epsilon = 23700$)	248 ($\epsilon = 9710$)
Piperidine	0.005			355 (broad) ($\epsilon = 28500$)		
Triethanolamine	0.015	479 ($\epsilon = 16600$)				
N,N-Dimethylformamide	0.005	499 ($\epsilon = 31100$)				
					325 ($\epsilon = 18600$)	
					330 (very broad, possibly 2 peaks) ($\epsilon = 19400$)	

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2. E. I. duPont de Nemours and Co., "Technical Information on duPont Explosives Specialties, Tacot, Properties," New York, N. Y.
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